



# A numerical model for a soluble lead-acid flow battery comprising a three-dimensional honeycomb-shaped positive electrode

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## HIGHLIGHTS

- New reactor for a soluble lead-acid flow battery with a honeycomb-shaped electrode.
- Simulation of the influence of the honeycomb dimensions on the cell characteristics.
- Experimental measurement of kinetic parameters for the  $\text{Pb}^{2+}/\text{Pb}$  and  $\text{PbO}_2/\text{Pb}$  systems.

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## ABSTRACT

A novel reactor design is proposed for the soluble lead-acid flow battery (SLFB), in which a three-dimensional honeycomb-shaped positive  $\text{PbO}_2$ -electrode is sandwiched between two planar negative electrodes. A two-dimensional stationary model is developed to predict the electrochemical behaviour of the cell, especially the current distribution over the positive structure and the cell voltage, as a function of the honeycomb dimensions and the electrolyte composition. The model includes several experimentally-based parameters measured over a wide range of electrolyte compositions. The results show that the positive current distribution is almost entirely determined by geometrical effects, with little influence from the hydrodynamic. It is also suggested that an increase in the electrolyte acidity diminishes the overvoltage during discharge but leads at the same time to a more heterogeneous reaction rate distribution on account of the faster kinetics of  $\text{PbO}_2$  dissolution. Finally, the cycling of experimental mono-cells is performed and the voltage response is in fairly good accordance with the model predictions.

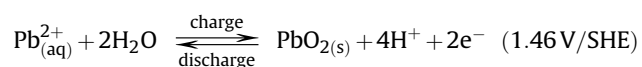
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## 1. Introduction

The soluble lead-acid flow battery (SLFB) has been developed over the last ten years as a possible low-cost solution for the stationary storage of electricity. As part of the redox flow batteries (RFBs), it involves solution-based electro-active species stored in an external electrolyte reservoir, but differs from the traditional RFBs in that it works with undivided cells since the same species (aqueous  $\text{Pb}^{2+}$ ) reacts at both electrodes. As a consequence, no ion-selective membrane is required, allowing the use of a single electrolyte, which commonly consists of a solution of lead methanesulfonate salt,  $\text{Pb}(\text{CH}_3\text{SO}_3)_2$ , in methanesulfonic

acid ( $\text{CH}_3\text{SO}_3\text{H}$ ). It is also different from numerous RFBs such as the all-vanadium or zinc-bromine systems because the reactants and products are not all soluble but, instead, solid phases are alternatively formed and dissolved during operation. These are lead dioxide ( $\text{PbO}_2$ ) at the positive electrode and lead ( $\text{Pb}$ ) at the negative electrode, deposited during the charge periods and dissolved back into the electrolyte during the discharge periods, according to the following reactions:

- at the positive electrode:

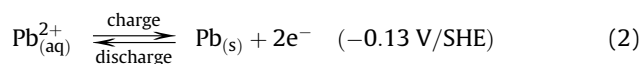


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- at the negative electrode:



So far, studies of the SLFB [1–10] have focused on mono-cells, or stack of cells, comprising two planar facing electrodes with the electrolyte flowing in-between. The charge efficiency of the system ( $\sim 80$ – $90\%$ ) is determined by the inability of lead dioxide to be completely dissolved after discharge. This phenomenon is most probably associated with the formation of complex oxides at the electrode surface [11]. The voltage and energy efficiencies are close to 75% and 60%, respectively, with a current density of  $20 \text{ mA cm}^{-2}$  and an inter-electrode gap of  $1.2 \text{ cm}$  [8]. These inefficiencies could be related to the sluggish kinetics associated with the deposition and dissolution of lead dioxide (reaction (1)), which induce significant overvoltages, in addition to the ohmic drops. Considering that, up to now, no solution has been found to improve the reversibility of reaction (1), the only possibility to decrease the charge transfer overvoltages seems to be a significant decrease in the current density. This implies a significant enhancement of the specific surface area of the positive electrode through the use of a three-dimensional matrix. The structure proposed here is a honeycomb matrix made up of hexagonal alveoli. A preliminary numerical study of the system could be of great assistance with choosing suitable dimensions and this is the subject of the present paper.

Several models (stationary or dynamic) of RFBs can be found in the literature, especially for the all-vanadium system. They are all based on mass, charge and momentum (transport) conservation equations combined with charge transfer kinetics relation at the electrodes. Examples for the all-vanadium technology are the transient 2-D model developed by Shah et al. [12] assessing the effect of variations in the species concentration, electrolyte flow and electrode porosity on the cell characteristics, or the 3-D model of Xu et al. [13] which studies various flow field designs for supplying electrolyte to the electrodes. In these studies, the microscopic scale of the electrodes porosity (usually made of carbon fibres) is statistically treated via additional terms in the mass transport equations. It affects the diffusion coefficients of the active species, the electrolyte and matrix conductivity as well as the electrolyte flow and, as a consequence, the concentration distribution of the soluble species and the performance of the battery.

Up to now, the soluble lead flow battery has been the subject of a single modelling attempt. The authors, Shah and co-workers [14], proposed a two-dimensional transient simulation of a mono-cell comprising  $10 \times 10 \text{ cm}^2$  planar electrodes, based on classical conservation laws and Butler–Volmer kinetics relations. The side (solid state) reaction involving  $\text{PbO}_x$  at the positive electrode during charge was considered in addition to the main liquid–solid reaction (1) and the kinetics parameters of each reaction were adjusted to capture the complex voltage transient of an experimental cell.

In the present paper, a two-dimensional stationary model of the SLFB is developed on the basis of a new reactor design, involving the three-dimensional honeycomb structure proposed for the positive electrode and two planar negative electrodes. It relies on the mass, charge and momentum conservation principles and on experiments specially conducted for determining some useful parameters (kinetics of reactions, electrolyte conductivity and electrochemical potentials). As opposed to the previous model of the SLFB, no time dependence is considered due to the fact that the voltage transient of the positive electrode appeared to be strongly influenced by morphological changes that arise at the surface of the  $\text{PbO}_2$  [15] and are not theoretically predictable. Rather, the purpose

of this study is to predict the main charge–discharge behaviour of the system (current densities, voltage components, species concentration...) over a wide range of electrolyte compositions and geometrical dimensions of the reactor. Because 3-D structures are generally associated to non-uniformities of the reaction rate over their surface owing to mass and charge transport limitations and leading to a non-fully or unbalanced utilization of the electrode, special attention is paid to study and quantify the uniformity of the current distribution on the positive electrode.

The innovative reactor design is presented in Section 2 together with the 2-D representation created for the simulations. The assumptions, the governing equations and boundary conditions are further presented and numerical details for the resolution are given. Section 3 contains details on the experiments conducted in this study. Section 4 presents the results of the preliminary experiments conducted to supply adequate parameters to the model. The simulation results are presented in Section 5. Firstly, assessments of the velocity field, ionic potential, species concentration and current density distributions throughout the entire reactor are reported. Then attention is drawn to the current distribution within the positive structure and to the cell voltage, studying the influence of the honeycomb dimensions (length and diameter of the alveoli) as well as of the electrolyte composition. Finally, a few results obtained with experimental flow cells are reported to illustrate the feasibility of the reactor and the data were compared to the model predictions.

## 2. Model

### 2.1. Geometry of the 3-D reactor

The reactor considered in this paper is a mono-cell made up of a high-specific surface area positive electrode and two negative electrodes. The positive electrode has a three-dimensional honeycomb structure consisting of a compact assembly of hexagonal crossing alveoli, or channels, and is sandwiched between two planar negative electrodes so that the channels of the positive electrode are perpendicular to the planes of the negative electrodes. A schematic representation of the mono-cell reactor is given in Fig. 1(a) together with a front view of the honeycomb electrode in Fig. 1(b). The electrolyte is supplied and released so that it can flow through the positive structure (flow-through configuration). For this purpose, holes can be drilled into the negative electrodes, as represented in Fig. 1(a). The electrolyte can also be supplied and/or released in the interelectrode gaps located on the bottom and the top faces, along the (x,y) plane, or on the vertical faces along the (x,z) plane.

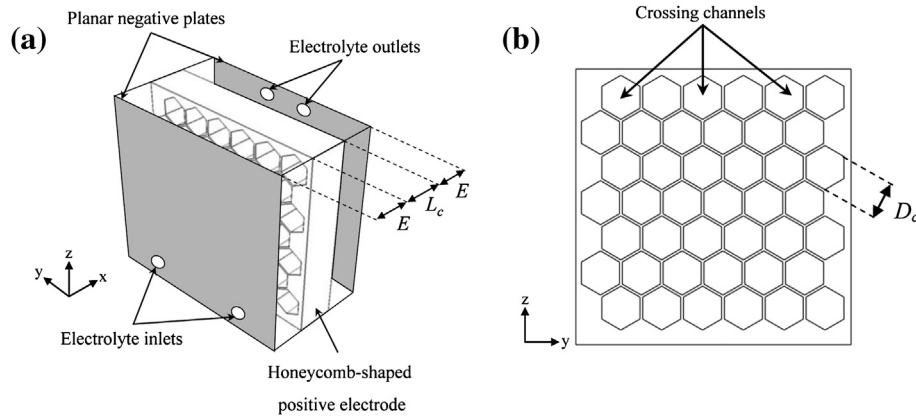
The three relevant dimensions of the reactor are: (1) the length of the channels, which is the thickness of the positive electrode along the x axis, referred to as  $L_c$ ; (2) the diameter of the channels, i.e. the distance between two opposite walls of the hexagons, referred to as  $D_c$ ; (3) the inter-electrodes distance  $E$ . The total area  $A^+$  developed by the positive electrode is the area  $A_c$  developed by the wall of each channel multiplied by the number  $N_c$  of channels:

$$A^+ = N_c A_c \quad (3)$$

Given that each of the six sides of the hexagons is  $D_c/\sqrt{3}$  in length,  $A_c$  is given by:

$$A_c = \frac{6D_c L_c}{\sqrt{3}} \quad (4)$$

The section  $S$  of the reactor in the (y,z) plane, which is also the area of the negative plates, divided by the section of each hexagon,



**Fig. 1.** (a) Schematic of the mono-cell reactor comprising a honeycomb-shaped positive electrode sandwiched between two planar negative electrodes. (b) Front view of the honeycomb structure.

which is  $3D_c^2/2\sqrt{3}$ , gives an approximation of the number  $N_c$  of channels:

$$N_c = \frac{2\sqrt{3}S}{3D_c^2} \quad (5)$$

The assumption is that the positive electrode is almost entirely paved with hexagons and that the wall separating two adjacent channels is negligible. Combining eq. (3) with (4) and (5) yields:

$$A^+ = \frac{4L_c S}{D_c} \quad (6)$$

Thus, the ratio  $R_A$  between the surface area of the positive electrode and the area of the two negative electrodes is given by:

$$R_A = \frac{A^+}{2S} = \frac{2L_c}{D_c} \quad (7)$$

This parameter is associated with the specific surface area of the positive electrode: it is higher when  $L_c$  is increased and/or  $D_c$  is decreased, i.e. when the channels are longer or thinner. During the operation of the cell, the average current density ratio between the positive and the negative electrodes equals  $R_A$ , that is, the average current density arising at the positive electrode surface will be  $R_A$ -times lower than that arising at the negatives plates. The total current crossing the cell is proportional to the average current density at the negative electrode, regardless of the honeycomb dimensions.

## 2.2. 2-D model for simulation

A numerical modelling of the entire 3-D reactor is very difficult to implement because the number of meshing elements required for significant precision would be far too high to be solved with a common processor. Instead, a two-dimensional representation of the system was created (Fig. 2), consisting of a simplified description of the 3-D reactor. For sake of simplicity, the honeycomb structure is represented as infinite parallel planes separated by the electrolyte. It comprises two main domains: the solid domains (electrodes) where the exclusive electronic transport takes place and the liquid domain (electrolyte) where both fluid mechanics and ionic transport are involved. The walls of the honeycomb structure are represented as thin horizontal and parallel rectangles (thickness  $\sim 0.2$  mm), perpendicular to the negative plates (thickness  $\sim 0.5$  mm). Thin vertical rectangular elements

are introduced at both extremities of the horizontal walls to ensure electrical connection of the positive structure. These artificial connectors are part of both solid and liquid domains: they act as electronics paths within the positive structure and they are transparent to the electrolyte flow. The electrolyte enters at the bottom left inter-electrodes space and is released at the upper right one, so that it can flow through the positive channels. The 2-D representation is then equivalent to a slice of the 3-D reactor in the  $(x,z)$  plane of Fig. 1(a), when the electrolyte is supplied along the bottom interelectrode gap and released along the opposite top interelectrode gap.

Using the same nomenclature as for the 3-D reactor, but with lowercase letter for the 2-D geometry, the total length  $L^+$  of the positive electrode–electrolyte interfaces is:

$$L^+ = 2n_c l_c \quad (8)$$

The length  $L^-$  of the negative electrode/electrolyte interfaces is 2 times the height of the 2-D reactor and can be written:

$$L^- = 2n_c d_c \quad (9)$$

Neglecting again the thickness of the positive wall elements, the length ratio  $R_L$  between  $L^+$  and  $L^-$  is:

$$R_L = \frac{L^+}{L^-} = \frac{l_c}{d_c} \quad (10)$$

which is two times lower than the surface ratio  $R_A$  calculated for the 3-D reactor (eq (7)). It is worth mentioning that the average current density ratio between the positive and the negative electrodes  $R_A$  is the most important parameter. Whatever the geometry, this parameter has to be maintained constant ( $R_L = R_A$ ). As a consequence the simulation of a 3-D reactor comprising the honeycomb dimensions  $L_c$  and  $D_c$  must be performed with the dimensions  $l_c = L_c$  and  $d_c = D_c/2$  in the 2-D model to respect the average current density ratio between positive and negative electrodes. Finally, the total current crossing the 2-D cell is proportional to the total length ( $2L^-$ ) of the negative plates.

## 2.3. Assumptions

The model is developed with the assumption of an infinite volume of the electrolyte reservoir so that the active species concentrations supplied to the reactor are constant. As a consequence, a steady state can be reached and the equations are

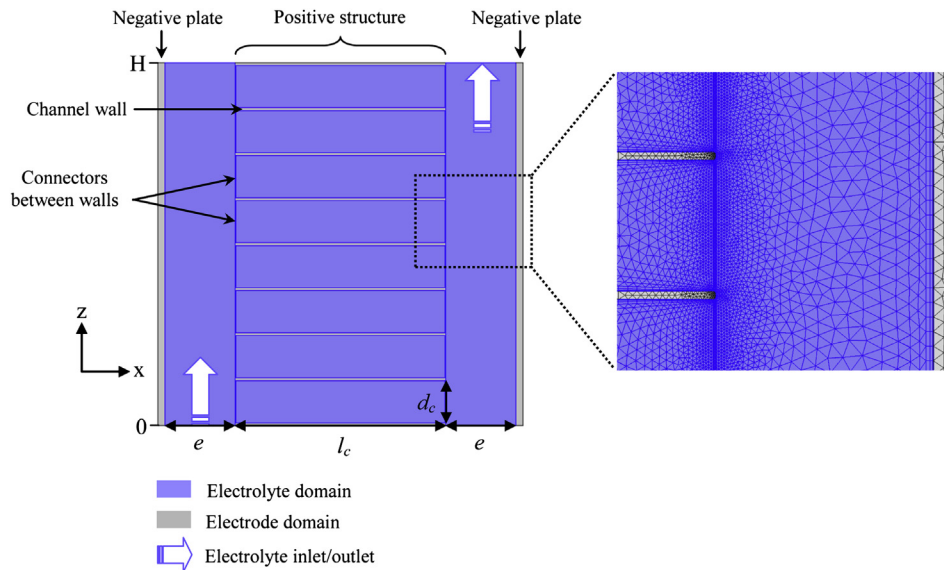


Fig. 2. Two-dimensional representation of the reactor used for the simulations with details on the meshing elements defined with Comsol Multiphysics.

solved in stationary conditions, without any time-dependent term. Five electrolyte composition were considered, lying between 1 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.25 \text{ M CH}_3\text{SO}_3\text{H}$  and 0.6 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1.05 \text{ M CH}_3\text{SO}_3\text{H}$  and corresponding to different states of charge (SOC). The input parameters depending on the composition are modified according to the experimental data described in Section 4.

The oxygen evolution reaction (OER) taking place during the deposition of  $\text{PbO}_2$  is not accounted for in the model, because the current associated is negligible compared to the main reaction, especially at low current density [11], and its kinetics is not easily determinable in the presence of lead(II) ions. The side reactions involving sub-oxides (mentioned  $\text{PbO}_x$  in the literature) are not considered. As a consequence, the Current vs. potential curves plotted for the  $\text{PbO}_2/\text{Pb}^{2+}$  couple were considered to be exclusively the result of the main reaction, i.e.  $\text{PbO}_2 \leftrightarrow \text{Pb}^{2+}$ . The changes in the local specific surface area of the  $\text{PbO}_2$  upon cycling, highlighted in a previous study [15], are also excluded from consideration due to the high complexity of the phenomenon. Instead, the  $\text{PbO}_2$  layer is assumed to have a compact surface morphology and the kinetics data included in the model were determined in these conditions. As a consequence, the simulated current distributions and voltages have sense exclusively when the compactness condition of  $\text{PbO}_2$  is fulfilled, that is, at the end of charge or at the beginning of discharge.

It is also assumed that the thicknesses of the Pb and  $\text{PbO}_2$  deposits are small compared to the reactor dimensions (diameter of channels, inter-electrode gap) so that they can be neglected. This assumption is particularly valid at the early stage of cycling, when a small amount of material has been accumulated at the electrode surface as a result of the incomplete dissolution of  $\text{PbO}_2$ .

## 2.4. Mass and charge balance equations

Having proposed a novel design for the SLFB, an electrochemical model was developed to simulate the flow of electrolyte, the transport of ionic species (reactants and products), the charge transport (electric current) through both the solid and the liquid phases, as well as the electrochemical reactions at the electrode

surfaces. The mass and charge balance equations are described below.

### 2.4.1. Governing equations

The flow of liquid electrolyte through the connected pore space is governed by the Navier–Stokes and the continuity equations given by:

$$\rho(\vec{u} \cdot \nabla) \vec{u} = -\nabla p + \mu \nabla^2 \vec{u} \quad (11)$$

$$\nabla \cdot \vec{u} = 0 \quad (12)$$

where  $\vec{u}$  is the liquid velocity field,  $p$  the pressure of the liquid,  $\rho$  its density and  $\mu$  its dynamic viscosity. Both  $\rho$  and  $\mu$  were taken as constant values (cf. Table 1). In the liquid phase, the transport of each species  $i$  is governed by the classical Nernst–Planck equation:

$$\vec{J}_i = -D_i \nabla c_i - \frac{z_i c_i D_i F}{RT} \nabla \phi + c_i \vec{u} \quad (13)$$

where  $c_i$  is the concentration of the species  $i$ ,  $\vec{J}_i$  its flux (in  $\text{mol m}^{-3} \text{ s}^{-1}$ ),  $D_i$  and  $z_i$  its diffusion coefficient and valence, respectively,  $\phi$  the ionic potential within the solution,  $F$  the Faraday constant,  $R$  the gas constant and  $T$  the temperature of the

Table 1

Values of constants related to the transport of charge and mass.

| Symbol                         | Quantity                                                                 | Value                                            |
|--------------------------------|--------------------------------------------------------------------------|--------------------------------------------------|
| $\sigma^+$                     | Conductivity of the positive electrode elements                          | $10^5 \text{ S m}^{-1a}$                         |
| $\sigma^-$                     | Conductivity of the negative electrodes                                  | $4.8 \times 10^6 \text{ S m}^{-1b}$              |
| $D_{\text{Pb}^{2+}}$           | $\text{Pb}^{2+}$ diffusion coefficient in the electrolyte [17]           | $0.94 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ |
| $D_{\text{H}^+}$               | Proton diffusion coefficient in the electrolyte [17]                     | $9.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  |
| $D_{\text{CH}_3\text{SO}_3^-}$ | $\text{CH}_3\text{SO}_3^-$ diffusion coefficient in the electrolyte [17] | $1.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  |
| $\mu$                          | Electrolyte dynamic viscosity                                            | $10^{-3} \text{ Pa s}$                           |
| $\rho$                         | Electrolyte density                                                      | $10^3 \text{ kg m}^{-3}$                         |

<sup>a</sup> Conductivity of  $\alpha\text{-PbO}_2$  [17].

<sup>b</sup> Conductivity of Pb [17].



electrolyte. A charge balance sets the divergence of the electrolyte current density  $\vec{j}$  ( $\vec{j} = F \sum_i z_i \vec{j}_i$ ) to zero leading to:

$$\nabla(\kappa \vec{\nabla} \phi) + F \sum_i z_i D_i \nabla^2 c_i = 0 \quad (14)$$

where the  $\kappa$  represents the conductivity of the electrolyte solution that depend on the  $\text{Pb}^{2+}$  and  $\text{H}^+$  concentrations. Eq. (14) includes the electroneutrality condition ( $\sum z_i c_i = 0$ ). For sake of simplicity,  $\kappa$  was considered as constant within the whole liquid domain and its value was assessed for a wide range of electrolyte compositions (see Fig. 3 and Table 2).

The electrode potential is thus expressed by a classical Ohm's law without any charge creation or consumption:

$$\vec{j}_s = -\sigma \vec{\nabla} V \quad (15)$$

where  $\vec{j}_s$  is the electronic current density in the solid phase,  $V$  is the electric potential and  $\sigma$  the conductivity of the solid phase considered.  $\sigma^+$  in the positive electrode domains and  $\sigma^-$  into the negative plates domains were set, respectively, equal to the lead dioxide and the lead conductivity (Table 1).

Table 1 summarizes the values of the solid phase's conductivities, diffusion coefficient of each active species and electrolyte viscosity and density that were used in the model, based on classical values reported in the literature. The boundary conditions that are required for the resolution of this system of equations on the entire model are described below.

#### 2.4.2. Boundary conditions

The electrolyte enters the reactor with a prescribed normal velocity  $v_{in}$  (in the  $z$  direction) and with a constant concentration  $c_i$  in each species. No-slip conditions ( $\vec{u} = 0$ ) are applied for the

electrolyte at the electrodes/electrolyte interfaces. The pressure  $p$  as well as the diffusive flux of all of the species ( $-D_i \vec{\nabla} c_i \cdot \vec{n}$ ) are set to zero at the outlet.

The rate at which species are generated or consumed at electrode–electrolyte active surfaces depends on their local faradaic current density at the electrolyte/electrode interface:

$$(\pm) \vec{j}_i \cdot \vec{n} = \frac{j^{+(-)}}{\nu_{ei} F} \quad (16)$$

where  $j^{+(-)}$  refer to the positive (negative) faradaic current density, respectively,  $\vec{n}$  is the normal vector of the electrode surface oriented towards the electrolyte and  $\nu_{ei}$ , the number of electron involved in the reaction per mole of reactant or product (i.e. 2 for  $\text{Pb}^{2+}$  and  $\text{PbO}_2$ ; 0.5 for  $\text{H}^+$ ). Charge transfer kinetics equations are expressed by using generalized Butler–Volmer expressions corresponding to tertiary current distributions, i.e. with concentration factors. These relations are written, with the corresponding (+) and (−) superscripts, as:

- at the positive electrode:

$$j^+ = i_0^+ \left( \frac{c_{\text{Pb}^{2+}}}{c_{\text{Pb}^{2+}}^*} e^{\alpha_0^+ n^+ f \eta^+} - \frac{c_{\text{H}^+}}{c_{\text{H}^+}^*} e^{-\alpha_r^+ n^+ f \eta^+} \right) \quad (17)$$

- at the negative electrode:

$$j^- = i_0^- \left( e^{\alpha_0^- n^- f \eta^-} - \frac{c_{\text{Pb}^{2+}}}{c_{\text{Pb}^{2+}}^*} e^{-\alpha_r^- n^- f \eta^-} \right) \quad (18)$$

where  $i_0$  is the exchange current density,  $\alpha_0$  and  $\alpha_r$  the symmetry factors in the oxidation and reduction direction, respectively,  $n$  the

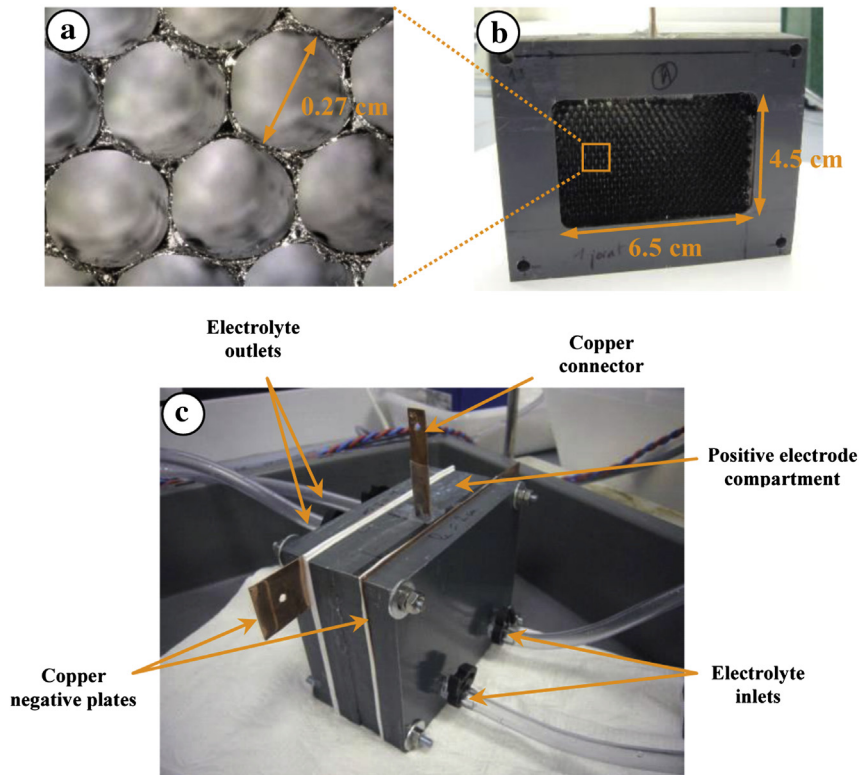


Fig. 3. (a) Microscopic observation of the glassy carbon honeycomb used as positive electrode; (b) honeycomb structure embedded in the PVC frame; (c) assembly of the mono-cell.

**Table 2**

Values of the experimental kinetics parameters and electrochemical potentials of the two electrochemical couples involved as a function of the electrolyte composition. Potential values are referred to an Ag/Ag<sub>2</sub>SO<sub>4</sub> reference electrode ( $E^0 = 0.65$  V vs. hydrogen).

| Electrolyte           |                     |                    | Pb <sup>2+</sup> /Pb system |                            | PbO <sub>2</sub> /Pb <sup>2+</sup> system |              |              |                    |                                 |
|-----------------------|---------------------|--------------------|-----------------------------|----------------------------|-------------------------------------------|--------------|--------------|--------------------|---------------------------------|
| [Pb <sup>2+</sup> ]/M | [H <sup>+</sup> ]/M | $\kappa/S\ m^{-1}$ | $i_0/\text{mA cm}^{-2}$     | $E_{th}^- (= E_{i=0}^-)/V$ | $i_0^+/\text{mA cm}^{-2}$                 | $\alpha_0^+$ | $\alpha_r^+$ | $E_{th}^+/V$       | $E_{i=0}^+/V$ (mixed potential) |
| 1                     | 0.25                | 12.0               | 145                         | −0.748                     | 0.144                                     | 0.243        | 0.282        | 0.888 <sup>a</sup> | 0.785                           |
| 0.9                   | 0.45                | 13.9               | 134                         | −0.765                     | 0.050                                     | 0.250        | 0.473        | 0.875 <sup>a</sup> | 0.829                           |
| 0.8                   | 0.65                | 17.8               | 122                         | −0.782                     | 0.038                                     | 0.260        | 0.572        | 0.883 <sup>a</sup> | 0.844                           |
| 0.7                   | 0.85                | 21.6               | 111                         | −0.79                      | 0.015                                     | 0.266        | 1.062        | 0.88 <sup>b</sup>  | 0.857                           |
| 0.6                   | 1.05                | 24.1               | 99                          | −0.797                     | 0.008                                     | 0.296        | 1.300        | 0.88 <sup>b</sup>  | 0.865                           |

<sup>a</sup> Experimentally determined by the Tafel lines intersection (Fig. 6(b)).

<sup>b</sup> Arbitrarily fixed (no Tafel line in dissolution).

number of electron(s) involved in the reaction,  $f$  is the ratio  $F/RT$ ,  $\eta$  the reaction overpotential and  $c_{\text{Pb}^{2+}}$  and  $c_{\text{H}^+}$  [resp.  $c_{\text{Pb}^{2+}}^*$  and  $c_{\text{H}^+}^*$ ] the concentrations of the species at the electrode/electrolyte interface [resp. in the electrolyte bulk].

The overpotentials are defined by:

$$\eta^{+(-)} = V^{+(-)} - E_{th}^{+(-)} - \phi \quad (19)$$

at the positive (negative) electrode.  $E_{th}^{+(-)}$  refers to the electrochemical potential of the positive (negative) electrode reaction. In order to make the model as predictable as possible, the kinetics parameters  $\alpha_0$  and  $\alpha_r$ , the exchange current density  $i_0$  as well as the electrochemical potential  $E_{th}$  were experimentally determined for both reactions as a function of the electrolyte composition (described in Section 4).

The reactor is simulated in galvanostatic conditions, which is the most common cycling mode for a battery. For this purpose, the current is recommended at the bottom and the top extremities of the positive electrode. Along these two inlet boundaries, a normal current density is then set to a value that is higher by a factor of  $n_c$  than the average current density ( $j^+$ ) desired at the positive electrode/electrolyte interfaces:

$$j_s^+(z=0, z=H) = n_c \langle j^+ \rangle = n_c \frac{\langle j^- \rangle}{R_L} \quad (20)$$

On the negative electrodes, the electrochemical potential is set at the top extremities:

$$V^-(z=H) = E_{th}^- \quad (21)$$

Finally, the ionic potential  $\phi$  is arbitrarily set to zero at the left negative electrode/electrolyte interface.

The absolute values of  $\phi$ ,  $V^+$  and  $V^-$  are not meaningful on their own and only the difference  $V^+ - V^-$  makes sense. It represents the cell voltage  $U$  that is calculated in the present case by the difference in the electrical potential taken at the top ends of the electrodes

$$U = V^+(z=H) - V^-(z=H) \quad (22)$$

It must be noted that  $U$  is the sum of the electromotive force, the electrochemical overpotentials associated to the electrodes reactions and the ohmic drops across the cell:

$$U = E_{th}^+ - E_{th}^- + \langle \eta^+ \rangle - \langle \eta^- \rangle + \langle \phi^+ \rangle - \langle \phi^- \rangle \quad (23)$$

where  $\langle \eta^+ \rangle$  (resp.  $\langle \eta^- \rangle$ ) refers to the average overpotential of the positive (resp. negative) electrode and  $\langle \phi^+ \rangle$  (resp.  $\langle \phi^- \rangle$ ) to the average ionic potential of the positive (resp. negative) electrode/electrolyte interface.

## 2.5. Numerical details

The model is implemented in *Comsol Multiphysics* (version 4.2a), which is an intuitive computational software particularly appropriate for models that involve several physics to be solved simultaneously.

The 2-D-geometry as in Fig. 2 is designed with the desired number and dimensions of channels. The fluid dynamics equations (11) and (12) were implemented in the liquid domain by the *Laminar Flow* toolbox and the *Electronic Currents* toolbox was used for defining the electronic transport equations in both electrodes (eq (15)) and the ionic potential equation in the liquid phase (eq (14)). The mass transport equations associated with each of the three ionic species were manually defined in the liquid phase by means of the general *Coefficient Form PDE* (Partial Differential Equation) toolbox. The geometry was then meshed using the *physics-controlled mesh* tool, setting the element size at 'finer'. A refined mesh was created at the electrode–electrolyte interfaces, associated to fast variable gradients, and at the edges of the positive electrode elements (see Fig. 2). There are approximately 5000 meshing elements per channel unit of the cell.

Due to the monodirectional coupling between fluid dynamics and mass transport (the electrolyte convection influences the transport of ionic species in solution but the opposite is false), it is not necessary to solve all of the equations simultaneously. Instead, the flow equations were solved independently and the velocity vector injected in the mass transport equations, which are solved all together with the liquid and solid phase potential equations, leading to a considerable saving in the computational time. Fully coupled non-linear solvers were employed each time. Direct linear solvers were employed, namely the *Pardiso* solver for fluidic equations and the *MUMPS* solver for electrochemical equations (default settings). The convergence criterion (error < 10<sup>−3</sup>) is reached typically after 15 s and five iterations for the resolution of the velocity field while the electrochemical variables are solved within a few minutes involving five to ten iterations.

## 3. Experimental details

### 3.1. Experiments for estimating the model parameters

Lead methanesulfonate–methanesulfonic acid electrolytes were prepared by dissolving lead oxide powder (PbO 99%, *Sigma–Aldrich*) in methanesulfonic acid solutions obtained by the dilution of MSA 70% from *Alfa Aesar*.

The conductivity measurements were performed with a *pPhenomenal CO11* graphite-electrode conductivity probe (2-electrode measurement) over a wide range of lead(II) and methanesulfonic acid concentrations. The probe was connected to a *Solartron SI 1250* impedancemeter that provided a sinusoidal AC signal (5 mV in amplitude) in the frequency range 65 kHz to 0.1 Hz.

The resistance across the probe was measured at the intersection of the Nyquist plot with the real impedance axis at high frequencies. The conductivity of the solution is given by the cell constant ( $k = 0.84$ ) divided by the resistance.

The electrodepositions of Pb and PbO<sub>2</sub> layers for the determination of the open circuit potentials as well as the kinetics plots were performed in 3-electrode cells, using a cylindrical platinum counter-electrode and an Ag|Ag<sub>2</sub>SO<sub>4</sub> ( $E^0 = 0.65$  V vs. hydrogen) reference electrode. A Solartron 1470 potentiostat/galvanostat monitored by CorrWare software was employed to provide current and measure the working electrode potential. The latter was a simple glassy carbon disc electrode (3 mm in diameter) for the open circuit potentials assessments and a rotating disc electrode (RDE) from Tacussel with a glassy carbon active surface (3 mm in diameter) for obtaining the kinetics plots under controlled diffusion conditions.

### 3.2. Experimental cells

The positive structure of the two experimental cells used in this study is made of a glassy carbon honeycomb structure obtained by the carbonisation, under nitrogen atmosphere, of an aramid matrix from Euro-Composites, according to the protocol described in Ref. [16]. The dimensions of the honeycomb cells are, after carbonisation,  $L_c = 1.4$  and  $1.8$  cm and  $D_c = 0.27$  cm for both cells (Fig. 3(a)), corresponding to a  $R_A$  ratios of 10.4 and 13.3 respectively. A copper tab is connected to the structure for the collection of current and the electrode is embedded in a PVC frame, leaving an exposed surface area of  $6.5 \times 4.5$  cm (Fig. 3(b)). Two copper plates are used as negative electrodes, separated from the positive structure with silicon gaskets (the inter-electrode gap  $E$  is 0.5 cm). The elements are assembled with two PVC plates applied at both ends and the clamping is provided by four threaded rods. The cell, connected with the two electrolyte inlets and outlets manifolds, is presented in Fig. 3(c). The electrolyte flow is provided by a KNF Lab Liquidport diaphragm pump with the flow rate set at  $\sim 300$  mL min<sup>-1</sup>. The galvanostatic cycling is recommended by a Biologic VSP-300 monitored by the EC-Lab software.

The electrolyte was made according to the same protocol as described in Section 3.1. 5 mM of hexadecyltrimethylammonium p-toluene sulfonate (C<sub>16</sub>H<sub>33</sub>(CH<sub>3</sub>)<sub>3</sub>N·C<sub>7</sub>H<sub>6</sub>SO<sub>3</sub>H) obtained from Sigma Aldrich was added to the solution as an additive for lead deposition at the negative electrode [5].

## 4. Experimental results for the model parameters

This section presents the results obtained for the estimation of several parameters that were used in the model equations: the electrolyte conductivity  $\kappa$ , the electrochemical potentials  $E_{th}$  and the kinetics parameters  $\alpha_o$ ,  $\alpha_r$ , and  $i_0$  associated to charge transfer at each electrode.

### 4.1. Electrolyte conductivity

Fig. 4 shows the evolution of the conductivity  $\kappa$  of 30 electrolytes containing lead methanesulfonate in the range 0–1.5 M and methanesulfonic acid in the range 0.1–1.5 M. As it can be seen,  $\kappa$  increases with the amount of acid when Pb(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> is kept at the same concentration. The latter has a more complex influence on the value of  $\kappa$ . For electrolytes containing a little amount of acid and lead(II),  $\kappa$  increases slightly with the concentration in the lead salt. A higher concentration in Pb(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> decreases the conductivity, especially if the electrolyte is strongly acidic. This increase in the electrolyte resistivity with the amount of lead(II) is consistent with the measures of Hazza et al. [1] and can be attributed to ions

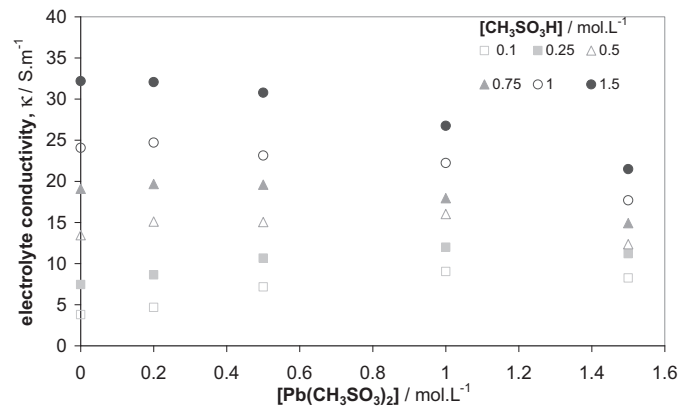


Fig. 4. Experimental values of the electrolyte conductivity as a function of the concentration in lead(II) ions, for several concentrations in methanesulfonic acid.

pairing. A fit based on the least squares method gives the following empirical relation:

$$\kappa \approx -4.23c_{Pb^{2+}}^2 + 9.89c_{Pb^{2+}} - 2.28c_{H^+}^2 + 23.75c_{H^+} - 7.55c_{Pb^{2+}}c_{H^+} + 2.12 \quad (24)$$

where  $\kappa$  is expressed in S m<sup>-1</sup> and the species concentrations are in mol L<sup>-1</sup>. This relation was used to approximate  $\kappa$  in eq (14) when simulating the cell with an inlet electrolyte composition whose conductivity was not measured experimentally.

### 4.2. Electrochemical potentials

The electrochemical potential of an electrochemical couple is commonly approximated by the Nernst equation. However, in the present case the calculated electrochemical potentials do not correctly match the experimental data and are then estimated as a function of the Pb<sup>2+</sup> and H<sup>+</sup> concentrations.

In the case of the Pb<sup>2+</sup>/Pb couple, the electrochemical potential corresponds to the open circuit potential of a lead electrode immersed in a Pb(II)–MSA solution because no additional reaction is expected to take place at the Pb surface.  $E_{th}^-$  was then assessed by measuring the open circuit potential of a lead-coated glassy carbon electrode in several electrolyte compositions (see Table 2). In the case of the PbO<sub>2</sub>/Pb<sup>2+</sup> couple, the open circuit potential of an PbO<sub>2</sub>-coated electrode immersed in a Pb(II)–MSA electrolyte is complicated by the oxygen evolution reaction taking place at the electrode surface. Indeed, the respective standard potentials of O<sub>2</sub>/H<sub>2</sub>O (1.23 V vs. H<sup>+</sup>/H<sub>2</sub>) and PbO<sub>2</sub>/Pb<sup>2+</sup> (1.46 V vs. H<sup>+</sup>/H<sub>2</sub>) allow the spontaneous reaction between H<sub>2</sub>O and PbO<sub>2</sub> leading to the formation of O<sub>2</sub> and Pb<sup>2+</sup>. This phenomenon is well-known at the positive plate of lead-acid batteries and results in the self-discharge of the system. It was also mentioned by Pletcher and Wills [3] as an explanation of the drop in the open-circuit voltage of the soluble lead flow battery after charge. The PbO<sub>2</sub> electrode potential is then, at open circuit, a mixed potential that is lower than the electrochemical potential (Table 2). The electrochemical potential  $E_{th}^+$  involved in eq (19) was obtained by mean of the intersection of the Tafel lines in the semi-log kinetics plots (described in Section 4.2).

It is worth mentioning that these experimental values of  $E_{th}$  may be biased by the liquid junction potential that may arise at the reference electrode/electrolyte interface. This junction potential would vary with the concentrations of active species and is very difficult to estimate. However, it is eliminated in the difference  $E_{th}^+ - E_{th}^-$  taken into account in the voltage  $U$  of the cell.

### 4.3. Kinetics parameters

Kinetics curves of the  $\text{Pb}^{2+}/\text{Pb}$  system were plotted by electrode potential scanning. Fig. 5 presents the Current density vs. Potential curve recorded in an electrolyte containing 0.5 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2$  + 0.5 M  $\text{CH}_3\text{SO}_3\text{H}$ , after correction of the ohmic drops. As it can be seen the dissolution of lead is a very fast process: the anodic current increases towards some maximum value. On the cathodic scan, the reaction rate is limited by the diffusion of  $\text{Pb}^{2+}$  ions and the curve is converging towards a limiting current of approximately  $-70 \text{ mA cm}^{-2}$ . In the cathodic scan, the current density can be expressed as:

$$j = \frac{i_0^- (e^{2\alpha_o f \eta^-} - e^{-2\alpha_r f \eta^-})}{1 - \frac{i_0^-}{i_l} e^{-2\alpha_r f \eta^-}} \quad (25)$$

where  $i_l$  is the limiting current density and all other symbols have the same significance as in eq (18), with  $n^- = 2$ . The electrochemical potential for defining  $\eta^-$  is the open circuit potential. The exchange current density  $i_0^-$  can be expressed, introducing the rate constant  $k_0$  of the reaction, as:

$$i_0^- = 2Fk_0(c_{\text{Pb}^{2+}})^{\alpha_o^-} \quad (26)$$

The least square method was used to fit the cathodic branch of several current density vs. overpotential curves recorded for several lead(II) concentrations at different rotation rates of the RDE. The assumption of  $\alpha_o^- + \alpha_r^- = 1$  has been made to reduce the degrees of freedom. The adjusted values obtained were, in average,  $k_0 \sim 3.5 \times 10^{-5} \text{ m s}^{-1}$  and  $\alpha_o^- \sim 0.78$  ( $\alpha_r^- \sim 0.22$ ). For the five electrolytes compositions considered in the study, the values of  $i_0^-$  to be used in eq (18) are deduced from eq (26) (see Table 2).

For the case of the  $\text{PbO}_2/\text{Pb}^{2+}$  system, the polarisation curves were recorded step by step in steady state conditions. The Current vs. Potential curves (corrected from ohmic drops) corresponding to the electrolyte compositions ranging from 1 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2$  + 0.25 M  $\text{CH}_3\text{SO}_3\text{H}$  to 0.6 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2$  + 1.05 M  $\text{CH}_3\text{SO}_3\text{H}$  are presented in a linear representation in Fig. 6(a) and in the semi-log Tafel representation in Fig. 6(b). As it can be seen, the electrolyte composition has a great influence on the polarization curves. When the ratio  $[\text{Pb}^{2+}]:[\text{MSA}]$  varies from 1:0.25 to 0.6:1.05, the cathodic branch of the polarization curves (dissolution of  $\text{PbO}_2$ ) is significantly shifted to higher potentials, reflecting the enhancement of the dissolution kinetics of lead dioxide on

account of the increase in the acid concentration (see also Ref. [15]). In the anodic branch ( $\text{PbO}_2$  deposition), the potential is also shifted to more positive values, though to a lesser extent. With such complex variations of the electrode kinetics, the relation (17) as well as the assumption  $\alpha_o^+ + \alpha_r^+ = 1$  were found to be no longer valid for the  $\text{PbO}_2/\text{Pb}^{2+}$  system. As a consequence, the parameters  $\alpha_o^+$ ,  $\alpha_r^+$  and  $i_0^+$  were estimated as follows for each electrolyte presented in Fig. 6, which are the electrolyte compositions used in the simulations.

The semi-log plots are linear for the electrolytes containing  $[\text{Pb}^{2+}]:[\text{H}^+]$  ratios of 1:0.25, 0.9:0.45 and 0.8:0.65. For these three electrolytes, the intersection between the cathodic and anodic lines gives the electrochemical potential  $E_{\text{th}}^+$  (close to 0.88 V) on the potential axis as well as the exchange current density  $i_0^+$  on the vertical axis. The slopes give estimated values for  $\alpha_o^+$  and  $\alpha_r^+$ . For the most acidic electrolytes ( $[\text{Pb}^{2+}]:[\text{H}^+] = 0.7:0.85$  and  $0.6:1.05$ ), the cathodic branch deviates from linearity as if the kinetics of dissolution were considerably accelerated. This is probably due to a change in the dissolution mechanisms, which is not the purpose of the present paper. As a consequence,  $i_0^+$ ,  $\alpha_r^+$ , and  $E_{\text{th}}^+$  cannot be obtained graphically for these electrolytes. Instead, a non-linear regression was performed, based on eq (24) without the concentration terms and with  $E_{\text{th}}^+$  fixed at 0.88 V.

Table 2 summarizes all of the experimental parameters estimated for both  $\text{PbO}_2/\text{Pb}^{2+}$  and  $\text{Pb}^{2+}/\text{Pb}$  couples in the electrolyte compositions ranging from  $[\text{Pb}^{2+}]:[\text{H}^+] = 1:0.25$  to  $0.6:1.05$ . The conductivity measured for each electrolyte is also given. As it can be seen there is at least a thousand-fold difference between the exchange current densities  $i_0^+$  and  $i_0^-$ , as a consequence of the very fast kinetics of  $\text{Pb}^{2+}/\text{Pb}$  compared to  $\text{PbO}_2/\text{Pb}^{2+}$ .

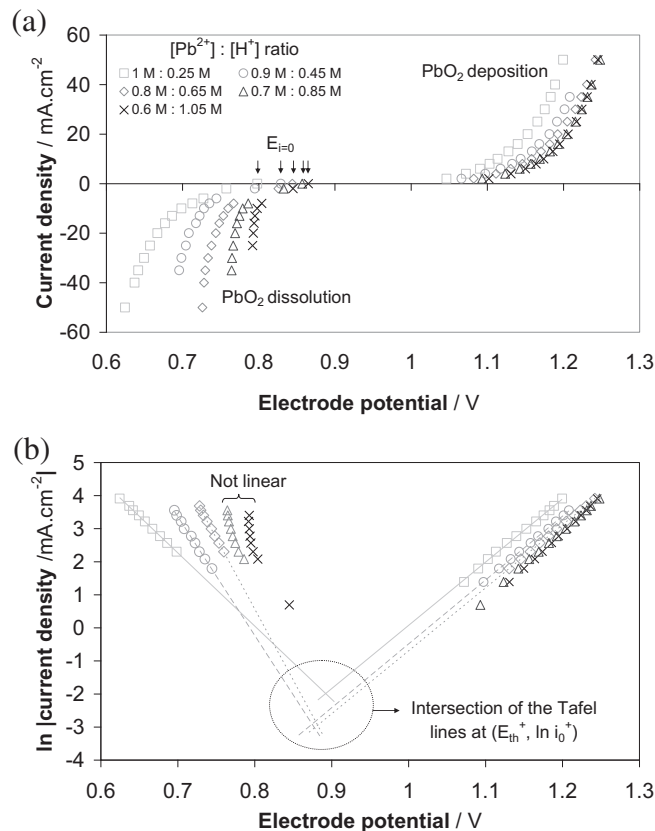


Fig. 6. Current vs. potential curves recorded for the deposition and dissolution of lead dioxide on a glassy carbon RDE (500 rpm) for several electrolyte compositions: (a) linear representation; (b) Tafel representation.

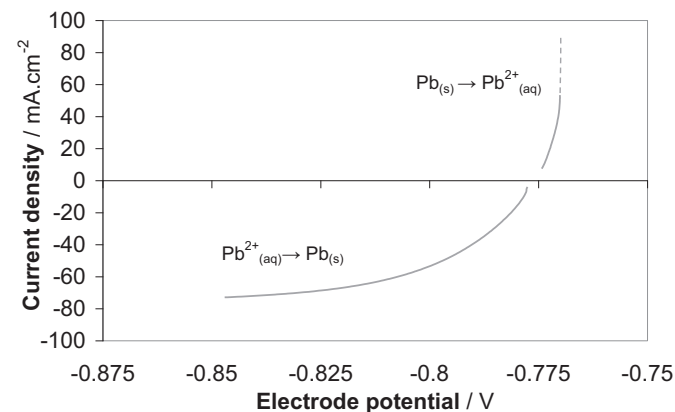
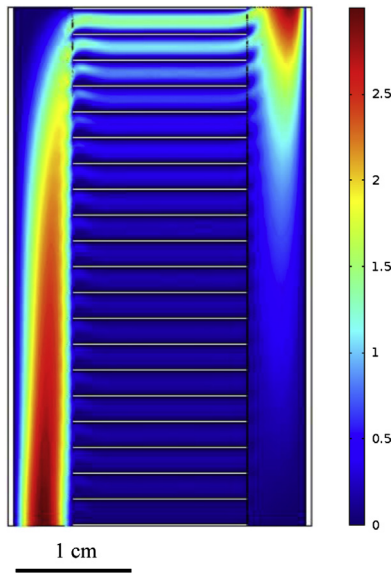


Fig. 5. Current density vs. potential curves (corrected from the ohmic drops) recorded for the deposition and dissolution of solid lead on a glassy carbon RDE (100 rpm). Electrolyte: 0.5 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2$  + 0.5 M  $\text{CH}_3\text{SO}_3\text{H}$ .





**Fig. 7.** Electrolyte velocity field (in  $\text{cm s}^{-1}$ ) within the 2-D representation comprising 20 channels. Average flow velocity prescribed at the bottom left:  $v_{\text{in}} = 2 \text{ cm s}^{-1}$ . Dimensions of the reactor:  $l_c = 1.5 \text{ cm}$ ,  $d_c = 0.20 \text{ cm}$ ,  $e = 0.5 \text{ cm}$ .

## 5. Results and discussion

### 5.1. Distributions of electrolyte flow, current and concentrations within the whole 2-D model

First simulations were performed to characterize the electrolyte flow, the current and active species concentration distributions at the macroscopic scale of the entire 2-D representation. The latter comprises 20 channels with dimensions  $l_c = 1.5 \text{ cm}$ ,  $d_c = 0.2 \text{ cm}$  and

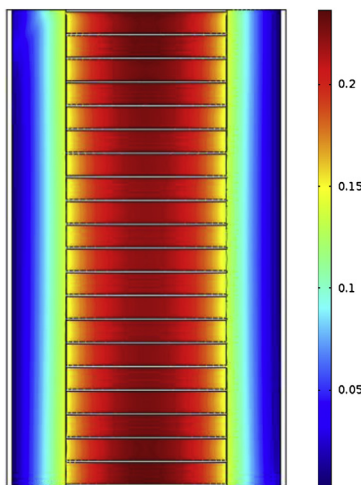
$e = 0.5 \text{ cm}$ . The corresponding 3-D diameter ( $D_c$ ) is  $0.4 \text{ cm}$ . The electrode length ratio  $L^+/L^-$  is 6.8, which is slightly lower than the ratio 7.5 calculated with eq (10), because of the thickness of the positive walls. The electrolyte, comprising  $1 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 0.25 \text{ M CH}_3\text{SO}_3\text{H}$ , enters the reactor with an average flow velocity of  $v_{\text{in}} = 2 \text{ cm s}^{-1}$ .

Fig. 7 shows the norm of the velocity vector  $\vec{u}$  of the electrolyte within the reactor. The flow appears quite heterogeneous, with a significant velocity in the left inter-electrodes space, where the electrolyte is supplied, compared to the one on the right. The electrolyte velocity is also heterogeneous within the positive structure. A few channels, that are situated at the top of the reactor, close to the outlet, are much more fed than the others. As it can be observed, the electrolyte flows slowly (few  $\text{mm s}^{-1}$ ) within a large majority of channels.

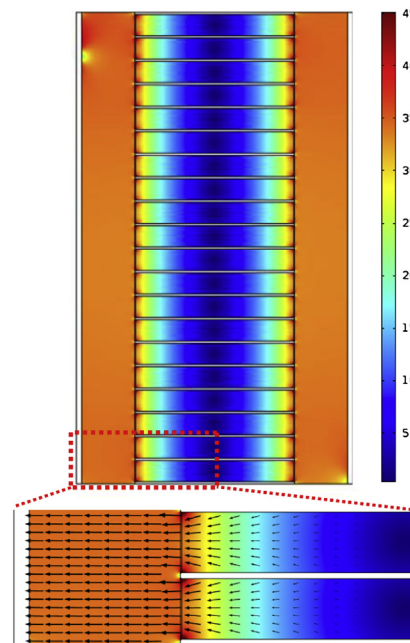
Fig. 8(a) presents the solution potential and Fig. 8(b) the norm of the current density within the electrolyte, in the case of charging the battery with a mean current density of  $5 \text{ mA cm}^{-2}$  at the positive electrode ( $-34 \text{ mA cm}^{-2}$  at the negative electrode). Both the solution potential and the current density display a quasi-symmetrical distribution around a vertical axis passing through the centre of the channels. While the current density is almost constant along the negative plates, it decreases from the ends to the centre of the channels as a result of the solution potential drops.

As shown in the current density profiles of Fig. 9 (simulated at the channel situated at the mid-height of the cell), if the cell is solicited at higher currents the reaction rate increases mainly at edges of the positive electrode, which makes the distribution more and more heterogeneous. The distribution is very similar from one channel to another. The difference arising in the current distributions between  $\text{PbO}_2$  deposition (charge) and dissolution (discharge) reflects the respective kinetics of these two processes and will be discussed in detail in Section 5.3.1. At the highest currents, however, a small asymmetry can be observed on the reaction rate at the positive structure: the current density is a little bit lower on the

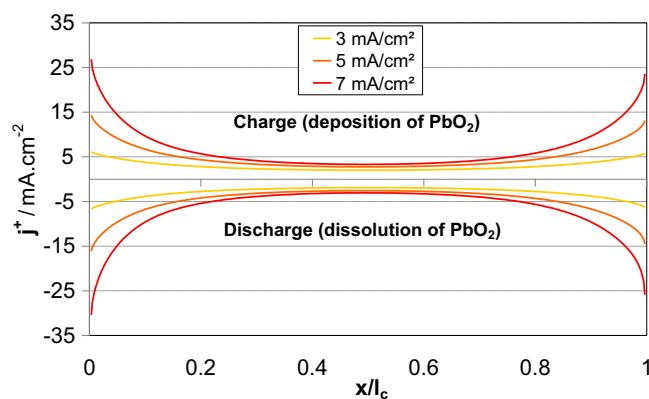
(a) Ionic potential (V)



(b) Electrolyte current density ( $\text{mA cm}^{-2}$ )



**Fig. 8.** (a) Ionic potential  $\phi$  (in V) and (b) norm of the current density vector  $\vec{j}$  in the electrolyte (in  $\text{mA cm}^{-2}$ ), simulated in the case of a charge at an average current density of  $+5 \text{ mA cm}^{-2}$  at the positive electrode ( $-34 \text{ mA cm}^{-2}$  at the negative plates). Dimensions of the reactor:  $l_c = 1.5 \text{ cm}$ ,  $d_c = 0.20 \text{ cm}$ ,  $e = 0.5 \text{ cm}$ . Prescribed average electrolyte velocity:  $v_{\text{in}} = 2 \text{ cm s}^{-1}$ . Electrolyte composition:  $1 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 0.25 \text{ M CH}_3\text{SO}_3\text{H}$ .



**Fig. 9.** Distribution of the reaction rate at the surface of a channel situated at mid-height of the 20-channel reactor, for three average current densities: ( $j^+$ ) = 3, 5 and 7 mA cm<sup>-2</sup> ( $j^-$ ) = 20, 34 and 48 mA cm<sup>-2</sup>). Electrolyte composition: 1 M Pb(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> + 0.25 M CH<sub>3</sub>SO<sub>3</sub>H. Same reactor dimensions as Figs. 7 and 8.

right side of the channels. This is due to the progressive consumption of the reactant species along the channel, in the direction of the electrolyte flow as it can be observed in Fig. 10 which presents the concentration fields of the Pb<sup>2+</sup> species during a charge in the same conditions as in Fig. 8. A similar depletion of the H<sup>+</sup> species during discharge can be observed, although to a lesser extent due to the higher diffusivity of protons compared to that of Pb<sup>2+</sup>. Also, a little depletion of reactants can be observed at the top left corner associated to small convection.

As all, the current distribution within the reactor appears to be mostly determined by the ohmic drops and kinetics with little effect on the transport of active species. It is therefore close to a secondary current distribution. This is mainly the result of the low current demand at the positive electrode, allowed by its high specific surface area, that leads to a small consumption of reactants.

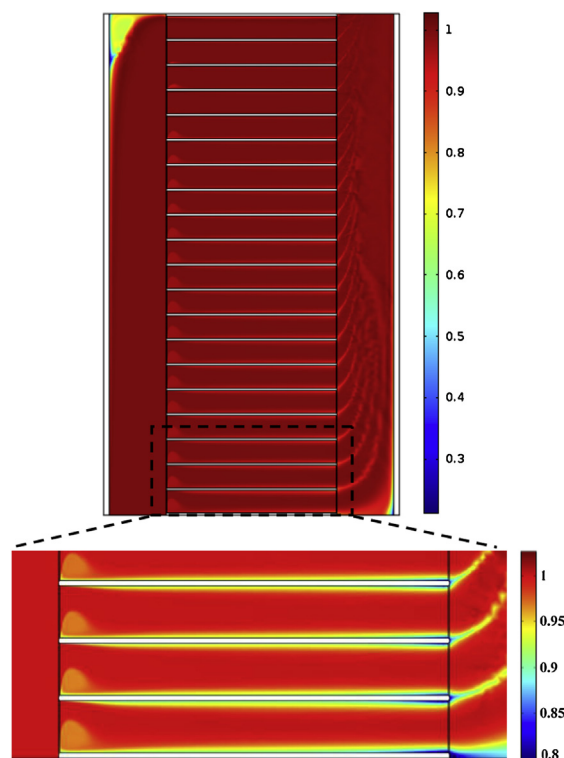
## 5.2. Effects of the honeycomb dimensions

In this section, where the effects of the honeycomb dimensions are assessed, the values of  $d_c$  and  $l_c$  are chosen so that the secondary-like distribution remains valid on the positive structure. In these conditions, the position of the channel on which the current distribution is studied is of no concern. The simulations were then performed with a smaller reactor (8 channels) in order to save computational time by decreasing the number of meshing elements.

### 5.2.1. Current distribution along the channels

A secondary current distribution is basically the result of two phenomena, which are: (1) the ohmic potential drops due to the electrolyte resistance and (2) the charge transfer resistance of the electrode kinetics. A uniform current is favoured when small ohmic drops occur, i.e. when a low current density crosses the electrolyte and/or the electrolyte has a high conductivity, or when the electrode kinetics is slow, i.e. when the reaction rate is poorly sensitive to the potential variation induced by the ohmic drops.

In the present cell, the honeycomb dimensions are expected to have a great influence on the current distribution on the positive structure.  $l_c$  determines in addition the distance over which the ohmic drops occur. Therefore, the distribution of  $j^+$  was simulated for several values of  $l_c$  and  $d_c$  in the 2-D model. Data are arbitrarily taken at the surface of a channel situated at mid-height of an 8-channel reactor. Current distributions are compared for the same average current density at the negative plates, i.e. for the same total current crossing the cell. The composition of the electrolyte is



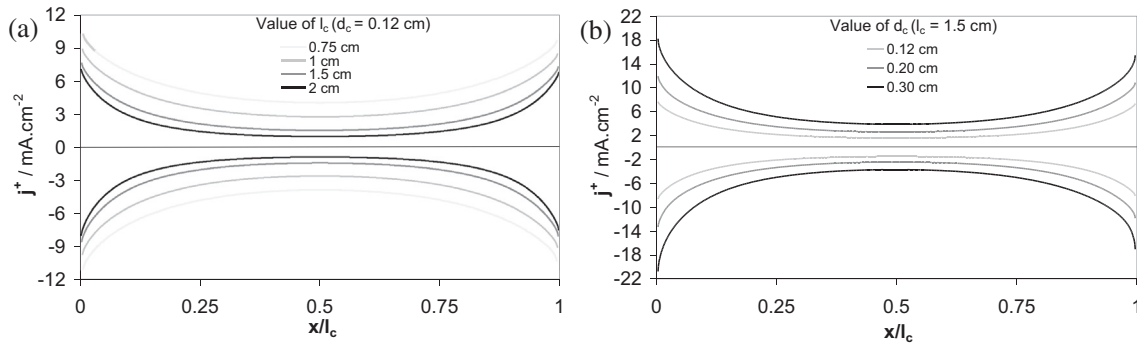
**Fig. 10.** Concentration field of the Pb<sup>2+</sup> species (in mol L<sup>-1</sup>) in the case of charging the cell at an average current density of 5 mA cm<sup>-2</sup> at the positive electrode ( $-34$  mA cm<sup>-2</sup> at the negative plates). Dimensions of the reactor:  $l_c = 1.5$  cm,  $d_c = 0.20$  cm,  $e = 0.5$  cm. Prescribed average electrolyte velocity:  $v_{in} = 2$  cm s<sup>-1</sup>. Electrolyte composition: 1 M Pb(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> + 0.25 M CH<sub>3</sub>SO<sub>3</sub>H.

again 1 M Pb(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> + 0.25 M CH<sub>3</sub>SO<sub>3</sub>H, corresponding to a low state of charge.

Fig. 11(a) reports the current distributions simulated at the surface of the honeycomb channel, along the  $x$  direction, during the charge and the discharge of the cell at ( $j^-$ ) = 30 mA cm<sup>-2</sup>, for four different values of  $l_c$  (0.75, 1, 1.5 and 2 cm) and with the diameter of channels being set at  $d_c = 0.12$  cm. The effect of the  $d_c$  is reported in Fig. 11(b) which presents the charge/discharge current distributions simulated at the same current for three values of  $d_c$  (0.12, 0.2 and 0.3 cm) and  $l_c$  being set at 1.5 cm.

It is clear that both the length and the diameter of the channels have a significant influence on the reaction rate distribution. When the length of the positive electrode is increased the average current density on its surface is decreased on account of the higher ratio  $R_L$ . The drop in current density observed from the edges to the centre of the channel is similar as can be seen in Fig. 11(a) ( $\sim 6$  mA cm<sup>-2</sup> during charge and  $\sim 7$  mA cm<sup>-2</sup> during discharge). The effect of the channel diameter is different. When it is increased, the average current density is higher due to the lower surface area developed by the positive electrode. A higher current density drop is also observed along the channels as can be seen in Fig. 11(b): from the edges to the centre,  $j^+$  drops, in charge, by approximately 6, 9 and 15 mA cm<sup>-2</sup> for  $d_c = 0.12$ , 0.2 and 0.3 cm respectively.

The uniformity of the reaction rate on the positive electrode must be quantified to select the most appropriate dimensions for the honeycomb structure. It is clear that a highly heterogeneous current profile along the channels would not be suitable since the edges would be much more solicited than the centre. On the contrary, a homogeneous distribution of the current leads to a better-balanced utilization of the positive electrode. The heterogeneity



**Fig. 11.** Current distributions along a channel, simulated for several honeycomb dimensions: (a) effect of the channel length with the diameter set at 0.12 cm; (b) effect of the channel diameter with the length set at 1.5 cm. Electrolyte composition: 1 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2$  + 0.25 M  $\text{CH}_3\text{SO}_3\text{H}$ . Prescribed current density:  $\pm 30 \text{ mA cm}^{-2}$  at the negative plates.

of the current density along the electrode can be defined as the extent to which the current deviates from its average, which would be the value in the ideal case of an infinitely conductive electrolyte. A dimensionless number  $\mathcal{H}$  quantifying the heterogeneity of the reaction rate along a channel can be defined as:

$$\mathcal{H} = \frac{\int_0^{l_c} |j^+ - \langle j^+ \rangle| dx}{\langle j^+ \rangle l_c} \quad (27)$$

The numerator represents the deviation of the current from the average value  $\langle j^+ \rangle$  while the denominator reports this deviation to the average value. Similarly, the  $\mathcal{H}$  number can be defined for quantifying the homogeneity:

$$\mathcal{h} = 1 - \mathcal{H} \quad (28)$$

A uniform current distribution, displaying very little deviation from its average value, is characterized by  $\mathcal{H} \sim 0$  and  $\mathcal{h} \sim 1$ . Conversely, a highly heterogeneous current yields  $\mathcal{H} \sim 1$  and  $\mathcal{h} \sim 0$ .

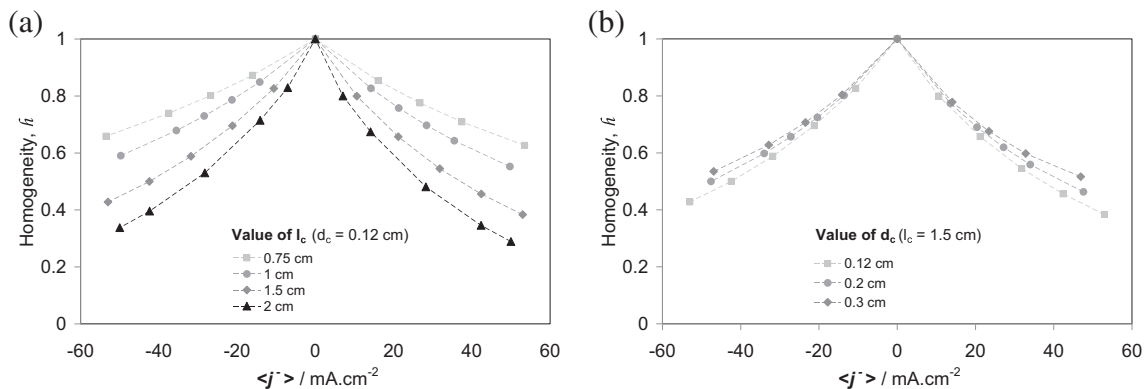
Fig. 12(a) and (b) presents the homogeneity number calculated for the positive current distributions as a function of the average current density  $\langle j^+ \rangle$  at the negative plates, when varying the parameters  $l_c$  and  $d_c$ , respectively. For a given  $\langle j^+ \rangle$ , increasing the length of channels leads to a significant loss of homogeneity. Indeed, the absolute current drop across the channel is similar, as stated before, but the average current density decreases when  $l_c$  is higher. As a consequence, the variation of  $j^+$  along the channels is higher with respect to its average value. On the contrary,  $d_c$  does not modify the homogeneity to a great extent. The higher absolute

current drops associated to the lower values of diameter are counterbalanced by a larger value of  $\langle j^+ \rangle$ , which results in a similar  $\mathcal{H}$  number. These results suggest that the depth of the honeycomb structure should be limited to avoid undesirable heterogeneities in the current distribution. At the same time, small channel diameter could maintain a reasonable specific surface area of the positive electrode without modifying much the current uniformity.

### 5.2.2. Cell voltage analysis

The variations of the cell voltage and of each of the two components of the overvoltage (charge transfer overpotentials and ohmic drops) upon the geometrical dimensions of the honeycomb electrode was assessed. The inter-electrode distance  $e$  (fixed at 0.5 cm) was not included in the varying parameters due to the fact that it solely contributes to the ohmic potential drops without influencing the charge transfer resistances. A longer inter-electrode distance shifts the charge voltage [resp. discharge voltage] to higher values [resp. to lower values] and vice versa, whereas the influence of the size (length and diameter) of the honeycomb elements on the cell voltage is not readily apprehensible since both ohmic drops and charge transfer components are affected independently. The electrolyte composition was again set at 1 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2$  + 0.25 M  $\text{CH}_3\text{SO}_3\text{H}$ . The reported overpotentials ( $\langle \eta^+ \rangle - \langle \eta^- \rangle$ ) include the contributions of both reactions but they are almost entirely determined by the reaction at the positive electrode ( $\langle \eta^+ \rangle$  is of the order of few mV).

Table 3 presents the simulated voltage data as a function of the applied current for the three lengths of channels 1, 1.5 and 2 cm and with a diameter set at 0.12 cm. As the positive structure gets deeper, the ohmic losses component increases on account of the longer



**Fig. 12.** Values of the number  $\mathcal{h}$ , quantifying the homogeneity of the current distribution along the channels, as a function of the current density at the negative plates, for several honeycomb dimensions: (a) effect of the channel length with the diameter set at 0.12 cm; (b) effect of the channel diameter with the length set at 1.5 cm. Electrolyte composition: 1 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2$  + 0.25 M  $\text{CH}_3\text{SO}_3\text{H}$ .

**Table 3**

Influence of the length of channel on the components of the cell voltage, with a diameter set at 0.12 cm.

| $\langle j^- \rangle / \text{mA cm}^{-2}$ | $l_c = 1 \text{ cm}, d_c = 0.12 \text{ cm} (R_L = 7.1)$      |            |      | $l_c = 1.5 \text{ cm}, d_c = 0.12 \text{ cm} (R_L = 10.6)$   |            |      | $l_c = 2 \text{ cm}, d_c = 0.12 \text{ cm} (R_L = 14.1)$     |            |      |
|-------------------------------------------|--------------------------------------------------------------|------------|------|--------------------------------------------------------------|------------|------|--------------------------------------------------------------|------------|------|
|                                           | $\langle \eta^+ \rangle - \langle \eta^- \rangle / \text{V}$ | IR drops/V | U/V  | $\langle \eta^+ \rangle - \langle \eta^- \rangle / \text{V}$ | IR drops/V | U/V  | $\langle \eta^+ \rangle - \langle \eta^- \rangle / \text{V}$ | IR drops/V | U/V  |
| 40                                        | −0.167                                                       | −0.208     | 1.26 | −0.145                                                       | −0.226     | 1.27 | −0.128                                                       | −0.241     | 1.27 |
| 30                                        | −0.154                                                       | −0.158     | 1.33 | −0.133                                                       | −0.174     | 1.33 | −0.118                                                       | −0.187     | 1.34 |
| 20                                        | −0.136                                                       | −0.107     | 1.40 | −0.116                                                       | −0.119     | 1.40 | −0.102                                                       | −0.129     | 1.41 |
| 0                                         | —                                                            | —          | 1.53 | —                                                            | —          | 1.53 | —                                                            | —          | 1.53 |
| −20                                       | 0.159                                                        | 0.107      | 1.91 | 0.136                                                        | 0.120      | 1.90 | 0.120                                                        | 0.131      | 1.89 |
| −30                                       | 0.182                                                        | 0.159      | 1.98 | 0.158                                                        | 0.175      | 1.97 | 0.141                                                        | 0.189      | 1.97 |
| −40                                       | 0.201                                                        | 0.209      | 2.05 | 0.177                                                        | 0.229      | 2.05 | 0.157                                                        | 0.245      | 2.04 |

distance created between the current collectors. At the same time, the average current density at the positive electrode is reduced due to the higher length ratio  $R_L$ , which lowers the charge transfer overpotentials associated mainly to the deposition and dissolution of lead dioxide. As a result, the cell voltage is found to be unchanged. The stability of the cell voltage upon changing the channels length was also observed in the other electrolyte compositions considered in this study.

Table 4 reports the simulated voltage data obtained with different values of  $d_c$  (0.12, 0.20 and 0.30 cm) and  $l_c$  set at 1.5 cm. It appears that the diameter of the alveoli has roughly no influence on the ohmic overvoltages, which are maintained, in the electrolyte 1 M  $\text{Pb}^{2+}/0.25 \text{ M H}^+$ , at 5.7 mV per each  $\text{mA cm}^{-2}$  prescribed at the negative plates. The charge transfer overpotential rises with the value of  $d_c$  due to the decrease in the length ratio  $R_L$  of the cell induced by larger channels, that is, due to the rise in the current density supplied at the positive electrode. Eventually, larger channels imply higher overvoltages leading to a shift in the cell voltage towards higher values in charge and lower values in discharge. The extent to which the voltage is modified is however limited: it does not exceed 50 mV for the range of currents and diameters investigated. These results suggest that the honeycomb dimensions may not be a key issue considering the cell voltage, which is likely to be much more significantly influenced by the morphological changes expected at the lead dioxide surface upon cycling.

### 5.3. Influence of the electrolyte composition

This section reports and discusses the effects of the electrolyte composition on the current distributions along the channels and on the simulated cell voltage and overvoltage components.

#### 5.3.1. Current distribution along the channels

When charging the battery, the electrolytic concentration of  $\text{Pb}^{2+}$  decreases and that of  $\text{H}^+$  increases. The kinetics associated with the positive electrode reaction as well as the electrolyte conductivity are strongly dependent on the electrolyte composition, as it was found in the preliminary experiments (see Figs. 4 and 6 and Table 2). As a consequence, the reaction rate distribution at

the positive electrode surface is expected to vary with the state of charge of the battery. Simulations of these variations are reported below.

Fig. 13(a) presents the evolution of the simulated current profiles along the channels ( $l_c = 1.5 \text{ cm}, d_c = 0.12 \text{ cm}$ ) as a function of the electrolyte composition, which ranges between 1 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.25 \text{ M CH}_3\text{SO}_3\text{H}$  and 0.6 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1.05 \text{ M CH}_3\text{SO}_3\text{H}$ . Both charge ( $\text{PbO}_2$  deposition,  $j^+ > 0$ ) and discharge ( $\text{PbO}_2$  dissolution,  $j^+ < 0$ ) are considered. The simulations were performed with an average current density set at  $\pm 3 \text{ mA cm}^{-2}$  at the positive electrode, corresponding to an average current of approximately  $\pm 30 \text{ mA cm}^{-2}$  at the negative plates ( $R_L \sim 10.6$ ). When the state of charge increases, i.e. when the lead(II) content decreases together with the increase in the acid content, the current distribution gets more homogeneous during deposition and more heterogeneous during dissolution. As in can be seen in Fig. 6 and as evidenced by the rapid evolution of  $\alpha^+$  in Table 2, the kinetics of the positive reaction is somewhat diminished during deposition and is significantly enhanced during dissolution when the electrolyte composition is getting more acidic. At the same time, the conductivity of the electrolyte rises significantly with the acidity (Fig. 4). In deposition, this induces more uniform current distributions (higher charge transfer resistance and smaller electrolyte resistance). In dissolution, the kinetics and electrolytes resistance evolutions with the composition have opposite trends on the current uniformity. However, towards lower  $\text{Pb}^{2+}$  and higher  $\text{H}^+$  contents, the heterogenization effect induced by the enhancement of the dissolution kinetics outweighs the homogenization effect of the conductivity enhancement and this leads to less uniform currents. Eventually, a two-fold difference in the absolute value of the current simulated at the ends of the channels appears between charge and discharge in the electrolyte comprising 0.6 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1.05 \text{ M CH}_3\text{SO}_3\text{H}$ .

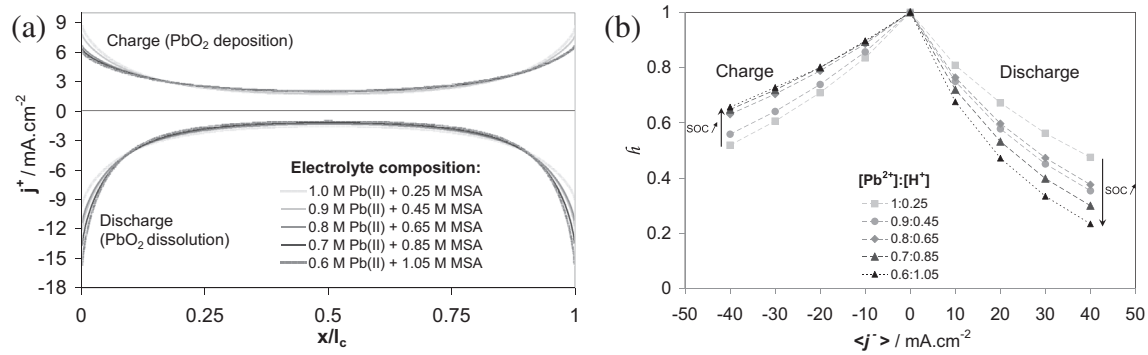
The homogeneity number  $\mathcal{H}$  calculated in charge and discharge with these electrolyte compositions are plotted vs.  $\langle j^- \rangle$  in Fig. 13(b). For a charge at a current density of  $30 \text{ mA cm}^{-2}$  at the negative electrodes (case of Fig. 13(a)),  $\mathcal{H}$  is 0.61 in the electrolyte 1 M  $\text{Pb}^{2+}/0.25 \text{ M H}^+$  and rises to 0.73 in the electrolyte 0.6 M  $\text{Pb}^{2+}/1.05 \text{ M H}^+$ , while in discharge  $\mathcal{H}$  is respectively 0.56 and 0.33 in these two electrolytes.

**Table 4**

Influence of the diameter of channel on the components of the cell voltage, with a length set at 1.5 cm.

| $\langle j^- \rangle / \text{mA cm}^{-2}$ | $l_c = 1.5 \text{ cm}, d_c = 0.12 \text{ cm} (R_L = 10.6)$   |            |      | $l_c = 1.5 \text{ cm}, d_c = 0.20 \text{ cm} (R_L = 6.8)$    |            |      | $l_c = 1.5 \text{ cm}, d_c = 0.30 \text{ cm} (R_L = 4.7)$    |            |      |
|-------------------------------------------|--------------------------------------------------------------|------------|------|--------------------------------------------------------------|------------|------|--------------------------------------------------------------|------------|------|
|                                           | $\langle \eta^+ \rangle - \langle \eta^- \rangle / \text{V}$ | IR drops/V | U/V  | $\langle \eta^+ \rangle - \langle \eta^- \rangle / \text{V}$ | IR drops/V | U/V  | $\langle \eta^+ \rangle - \langle \eta^- \rangle / \text{V}$ | IR drops/V | U/V  |
| 40                                        | −0.145                                                       | −0.226     | 1.27 | −0.170                                                       | −0.226     | 1.24 | −0.195                                                       | −0.229     | 1.22 |
| 30                                        | −0.133                                                       | −0.174     | 1.33 | −0.157                                                       | −0.173     | 1.31 | −0.179                                                       | −0.174     | 1.29 |
| 20                                        | −0.116                                                       | −0.119     | 1.40 | −0.138                                                       | −0.118     | 1.38 | −0.158                                                       | −0.119     | 1.36 |
| 0                                         | —                                                            | —          | 1.53 | —                                                            | —          | 1.53 | —                                                            | —          | 1.53 |
| −20                                       | 0.136                                                        | 0.120      | 1.90 | 0.161                                                        | 0.118      | 1.92 | 0.184                                                        | 0.119      | 1.94 |
| −30                                       | 0.158                                                        | 0.175      | 1.97 | 0.184                                                        | 0.174      | 2.00 | 0.209                                                        | 0.175      | 2.02 |
| −40                                       | 0.177                                                        | 0.229      | 2.05 | 0.203                                                        | 0.227      | 2.07 | 0.230                                                        | 0.229      | 2.1  |





**Fig. 13.** Effect of the electrolyte composition (state of charge, SOC) on the current distribution along the channels: (a) current density distributions for an average current density ( $\langle j^* \rangle$ ) of  $\pm 30 \text{ mA cm}^{-2}$  at the negative plates ( $\langle j^+ \rangle$  of  $\pm 3 \text{ mA cm}^{-2}$ ); (b) evolution of the homogeneity with the species concentration. Dimensions of the reactor:  $l_c = 1.5 \text{ cm}$ ,  $d_c = 0.12 \text{ cm}$ ,  $e = 0.5 \text{ cm}$ .

The consequence of such differences in the current uniformity between charge and discharge could impact the thickness of lead dioxide along the channels of the positive electrode. After a first charge, the thickness profile is expected to follow the charging current distribution of Fig. 13(a), with a thicker deposit at the edges of the channels. At the following discharge, the discharging current profiles of Fig. 13(a) suggests that lead dioxide will be dissolved much faster at the edges than in the centre of the channels, especially if the electrolyte contains a high amount of acid. This can result in a deletion of active materials first at the edges followed by a shrinking of the remaining active  $\text{PbO}_2$  in the inner part of the positive electrode. In this situation, the average distance between the negative electrodes and the active part of the positive electrodes will be longer which would imply additional ohmic drops. This may be avoided by decreasing the discharge current compared to the charge current in order to equilibrate the uniformity number of the distributions between charge and discharge.

### 5.3.2. Cell voltage analysis

Table 5 summarizes the values of the cell voltages and the overvoltage components simulated for three  $[\text{Pb}^{2+}]:[\text{H}^+]$  ratios: 1:0.25, 0.8:0.65 and 0.6:1.05. The honeycomb dimensions are  $l_c = 1.5 \text{ cm}$  and  $d_c = 0.12 \text{ cm}$  with an inter-electrode distance  $e = 0.5 \text{ cm}$ . The open circuit voltages expected for these three electrolytes, are also given, based on the open circuit measurements performed separately for each couple (see Table 2). The effect of the electrolyte composition on the voltage data is significant. Either in charge or in discharge, the enhancement of the electrolyte conductivity with the increase in the acidity leads to lower ohmic

drops overvoltages. The voltage losses or gains due to the electrolyte resistance are  $\pm 5.7$ , 3.9 and 2.8 mV per each  $\text{mA cm}^{-2}$  prescribed at the negative plates, for the electrolytes containing the concentration ratios of 1:0.25, 0.8:0.65 and 0.6:1.05, respectively. The contribution of the charge transfer depends on the regime. In the case of a charge, the overpotentials are more significant for electrolytes containing low  $[\text{Pb}^{2+}]:[\text{H}^+]$  ratios, due to the slower kinetics of lead dioxide deposition. The opposite trend is obtained when the cell is discharged owing to the more straightforward dissolution of  $\text{PbO}_2$  in acidic media. Eventually, when the electrolyte evolves towards low  $[\text{Pb}^{2+}]:[\text{H}^+]$  ratios and for a given current prescribed at the negative electrodes, the simulated cell voltage rises slightly for a charge regime and drops significantly for a discharge regime.

### 5.4. Experimental cells and comparison with the model

In this section a few results obtained with the experimental cells described in Section 3.2 are reported. On one hand, the aspect of the lead dioxide deposited on the honeycomb is studied after a first charge. On the other hand, the voltage response of another experimental cell is presented and compared with the voltage predicted by the model.

#### 5.4.1. Aspect of the $\text{PbO}_2$ deposit after a charge

A first charge of the experimental cell comprising alveoli dimensions of  $L_c = 1.8 \text{ cm}$  and  $D_c = 0.27 \text{ cm}$  ( $R_A \sim 13$ ) was performed in order to characterize the aspect of the lead dioxide deposit on the honeycomb glassy carbon. The cell was charged for 3 h at an average current density of  $-20 \text{ mA cm}^{-2}$  at the negative plate (1.2 A

**Table 5**

Evolution of the simulated cell voltage and of the charge transfer and ohmic drops components with the current prescribed and the electrolyte composition. Dimensions of the reactor:  $l_c = 1.5 \text{ cm}$ ,  $d_c = 0.12 \text{ cm}$ ,  $e = 0.5 \text{ cm}$ .

| $\langle j^- \rangle / \text{mA cm}^{-2}$ | $\langle j^+ \rangle / \text{mA cm}^{-2}$ | $[\text{Pb}^{2+}]:[\text{MSA}] = 1:0.25$                     |            |      | $[\text{Pb}^{2+}]:[\text{MSA}] = 0.8:0.65$                   |            |      | $[\text{Pb}^{2+}]:[\text{MSA}] = 0.6:1.05$                   |            |      |
|-------------------------------------------|-------------------------------------------|--------------------------------------------------------------|------------|------|--------------------------------------------------------------|------------|------|--------------------------------------------------------------|------------|------|
|                                           |                                           | $\langle \eta^+ \rangle - \langle \eta^- \rangle / \text{V}$ | IR drops/V | U/V  | $\langle \eta^+ \rangle - \langle \eta^- \rangle / \text{V}$ | IR drops/V | U/V  | $\langle \eta^+ \rangle - \langle \eta^- \rangle / \text{V}$ | IR drops/V | U/V  |
| Discharge                                 |                                           |                                                              |            |      |                                                              |            |      |                                                              |            |      |
| 40                                        | −3.8                                      | −0.145                                                       | −0.226     | 1.27 | −0.100                                                       | −0.147     | 1.42 | −0.072                                                       | −0.105     | 1.50 |
| 30                                        | −2.8                                      | −0.133                                                       | −0.174     | 1.33 | −0.094                                                       | −0.114     | 1.46 | −0.068                                                       | −0.081     | 1.53 |
| 20                                        | −1.9                                      | −0.116                                                       | −0.119     | 1.40 | −0.085                                                       | −0.078     | 1.50 | −0.063                                                       | −0.056     | 1.56 |
| Open circuit                              |                                           |                                                              |            |      |                                                              |            |      |                                                              |            |      |
| 0                                         | 0                                         | —                                                            | —          | 1.53 | —                                                            | —          | 1.63 | —                                                            | —          | 1.66 |
| Charge                                    |                                           |                                                              |            |      |                                                              |            |      |                                                              |            |      |
| −20                                       | 1.9                                       | 0.136                                                        | 0.120      | 1.90 | 0.191                                                        | 0.082      | 1.94 | 0.233                                                        | 0.061      | 1.97 |
| −30                                       | 2.8                                       | 0.158                                                        | 0.175      | 1.97 | 0.218                                                        | 0.121      | 2.00 | 0.263                                                        | 0.090      | 2.03 |
| −40                                       | 3.8                                       | 0.177                                                        | 0.229      | 2.05 | 0.243                                                        | 0.158      | 2.07 | 0.300                                                        | 0.118      | 2.10 |

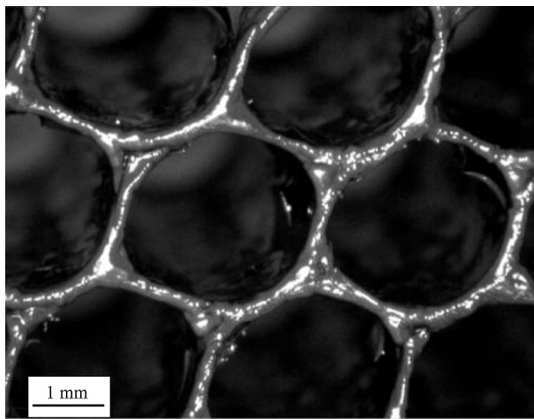
applied to the cell), using an electrolyte comprising 1 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.25 \text{ M CH}_3\text{SO}_3\text{H}$  (+5 mM of additive) in the uncharged state. At the end of charge, the cell was thoroughly rinsed with water and disassembled for examining the positive electrode at the optical microscope.

The aspect of lead dioxide can be seen in the picture of Fig. 14. The deposit appears compact, well-adherent and is uniformly distributed, as predicted in Section 5.1, along the plane perpendicular to the channel axis [(y,z) plane of Fig. 1]. Using edge views of the honeycomb such as that of Fig. 14, it is possible to evaluate the thickness of lead dioxide that was deposited at the extremities of the channels and to compare with the model predictions. Several measurements performed at different locations of the electrode gave an average value of  $50 \mu\text{m}$ . The modelling of the reaction rate distribution in an ad hoc 2-D representation ( $l_c = 1.8 \text{ cm}$ ,  $d_c = 0.12 \text{ cm}$  and  $R_L = 13$ ) gives a current density of  $3.2 \text{ mA cm}^{-2}$  at the edges of the positive electrode with an average value of  $1.5 \text{ mA cm}^{-2}$ . Given the charging time (3 h), this implies the growth of  $44 \mu\text{m}$  of  $\text{PbO}_2$  at the edge ( $20 \mu\text{m}$  in average), which is in good accordance with the microscopic observations. Further observations are planned to characterize the morphology of lead dioxide during cycling.

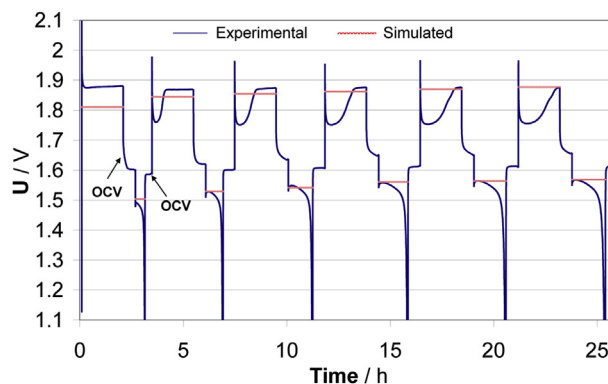
#### 5.4.2. Voltage response

The other experimental cell ( $l_c = 1.4 \text{ cm}$ ) was cycled with an average current density of  $10 \text{ mA cm}^{-2}$  at the negative plates ( $0.6 \text{ A}$  prescribed to the cell). The charging steps lasted 2 h and the discharges were applied until the potential dropped to  $0.6 \text{ V}$ . The cell was kept at open circuit for 30 min between each charge/discharge period. The electrolyte composition was, in the uncharged state, 1 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.25 \text{ M CH}_3\text{SO}_3\text{H}$  (+5 mM of additive). The electrolyte volume was  $0.5 \text{ L}$ , so that the charge periods imply a decrease of  $-0.09 \text{ M}$  in the lead(II) concentration and an increase of  $+0.18 \text{ M}$  in the acid concentration.

The honeycomb was represented in the model with the same depth ( $l_c = 1.4 \text{ cm}$ ) and with a channel diameter  $d_c = 0.12 \text{ cm}$  to set a length ratio  $R_L$  corresponding to the area ratio  $R_A$  of the cell (10.4). The voltages were simulated taking into account the derivation of the species concentrations throughout cycling (less  $\text{Pb}^{2+}$  and more  $\text{H}^+$  due to the incomplete discharges). Due to the fact that the electrolyte compositions available in Table 2 are defined by steps of  $0.1 \text{ M}$  of  $\text{Pb}^{2+}$ , interpolations of the simulated data are necessary. For example, the first charge occurs with an electrolyte composition ratio evolving between 1:0.25 (beginning of charge) and



**Fig. 14.** Optical microscope picture of the lead dioxide deposited at the surface of the glassy carbon honeycomb after a 3 h-charge at  $(j^-) = -20 \text{ mA cm}^{-2}$ . Honeycomb dimensions:  $l_c = 1.8 \text{ cm}$ ,  $d_c = 0.27 \text{ cm}$ . Electrolyte composition before charge: 1 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.25 \text{ M CH}_3\text{SO}_3\text{H}$ .



**Fig. 15.** Voltage response of the experimental cell compared with simulations. Current density:  $10 \text{ mA cm}^{-2}$  at the negative plates. Electrolyte composition in the uncharged state: 1 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.25 \text{ M CH}_3\text{SO}_3\text{H}$ .

0.91:0.43 (end of charge), which gives an average composition ratio of  $\sim 0.95:0.35$ . The predicted voltage was then obtained by averaging between the two voltages simulated in the electrolytes ratios 1:0.25 and 0.9:0.45.

The internal resistance of the experimental cell (assessed by EIS measurement) is  $0.11 \Omega$  before the first charge while the simulation of the ohmic drops gives an internal resistance of  $0.095 \Omega$ , close to the experimental value. The voltage response of the first six cycles is shown in Fig. 15 together with the voltages simulated by the model for each cycle. The voltage transient displays the classical profile reported for planar-electrode SLFB reactors, comprising charging steps with a first lower voltage period followed by a rise of the voltage to a plateau. As mentioned previously, the numerical predictions make sense exclusively for the first charge, for the final plateaus of the subsequent charging steps and for the beginning of the discharging steps, i.e. when lead dioxide is expected to have a compact surface morphology. As it can be seen there is a pretty good accordance between experimental and simulated voltages for these periods. The progressive increase in the discharge voltage upon cycling is particularly well captured by the model. This must be related to variation in the electrolyte composition, evolving towards more acidity (see Table 5). The estimated electrolyte composition after the 6th cycle is indeed  $0.77 \text{ M Pb(II)}:0.71 \text{ M MSA}$ . Discrepancies between predicted and measured voltages, especially for the first charge, can be due to contact resistances or potential losses in the glassy carbon structure which is not as good conductive as copper, lead or lead dioxide.

Further study of the reactor will be necessary, especially concerning the poor completeness of the discharging periods. Investigations will focus, for instance, on the effect of the discharging current (Section 5.3.1) and on the role played by  $\text{PbO}_x$ .

## 6. Conclusion

A new cell design has been proposed for the soluble lead-acid methanesulfonic redox-flow battery, in which the  $\text{PbO}_2$ -positive electrode has a honeycomb-shaped structure and is sandwiched between two planar Pb-negative plates and a steady-state two-dimensional experimental-based numerical model has been developed to simulate the basic features expected for the operation of this mono-cell. The simulations basically focus on predictions of the current distributions at the surface of the honeycomb alveoli with quantification of their heterogeneities and on prediction of the cell voltage. Some data were successfully compared with experimental results obtained with homemade cells.

The model results can be summarized as follows:

- A quasi-secondary current distribution is predicted within the cell, with little mass transport effects, as long as a reasonable current is prescribed to the cell. The distribution of the reaction rate along the positive channels, defined by the competitive effects between ohmic drops and electrode kinetics, is quasi-symmetric with the highest values located at the edges. Heterogeneities are favoured at high current regimes.
- The length  $l_c$  of the channels has a significant impact on the positive current uniformity. For the same current applied to the cell, more heterogeneous currents are expected when increasing  $l_c$  this suggests that the latter must be limited. On the other hand,  $l_c$  was found to have no significant impact on the cell voltage due to compensatory effects on the ohmic and the charge transfer overvoltages.
- The diameter  $d_c$  of the honeycomb channels modifies the positive current distribution without changing significantly the heterogeneity. It modifies slightly the cell voltage: lower overvoltages are expected with small values of  $d_c$ . This suggests that the honeycomb alveoli can be chosen significantly small.
- The electrolyte composition, due to its influence on both the  $\text{PbO}_2$  kinetics and the electrolyte conductivity, is expected to modify the positive current distributions as well as the cell voltage. Electrolytes comprising low  $\text{Pb}^{2+}$  and high  $\text{H}^+$  contents, lead to slightly more uniform current distributions in charge and significantly more heterogeneous ones in discharge. This can result in the early depletion of  $\text{PbO}_2$  from the edge of the channels during discharge, which could be avoided by discharging the cell at a lower current. The cell voltage is expected to be slightly higher during charge and significantly higher during discharge in low  $\text{Pb}^{2+}$ /high  $\text{H}^+$  electrolytes.

Finally, the cycling of the experimental cells showed good accordance with the model predictions regarding for example the thickness of the  $\text{PbO}_2$  deposited at the edge of the channels after a charge as well as the voltage response. The need for more investigation on this new reactor design and the electrode material is however suggested, especially concerning the poor dissolution of lead dioxide.

## Acknowledgements

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## Symbols

### Latin letters

|           |                                                                              |
|-----------|------------------------------------------------------------------------------|
| $A^+$     | total surface area developed by the 3-D honeycomb structure ( $\text{m}^2$ ) |
| $A_c$     | wall area of each honeycomb channel ( $\text{m}^2$ )                         |
| $c$       | electrolyte concentration ( $\text{mol m}^{-3}$ )                            |
| $D$       | diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )                         |
| $d_c$     | channel diameter in the 2-D representation (m)                               |
| $D_c$     | channel diameter in the 3-D honeycomb structure (m)                          |
| $e$       | inter-electrode distance in the 2-D representation (m)                       |
| $E$       | inter-electrode distance in the 3-D representation (m)                       |
| $E_{i=0}$ | open circuit potential of the electrode (V)                                  |
| $E_{th}$  | electrochemical potential (V)                                                |

|               |                                                                                                               |
|---------------|---------------------------------------------------------------------------------------------------------------|
| $f$           | $F/RT$ ( $\text{V}^{-1}$ )                                                                                    |
| $F$           | Faraday constant ( $96485 \text{ C mol}^{-1}$ )                                                               |
| $H$           | reactor height in the 2-D representation (m)                                                                  |
| $\mathcal{H}$ | dimensionless number quantifying the homogeneity of the current distribution ( $0 < \mathcal{H} < 1$ )        |
| $\mathcal{H}$ | dimensionless number quantifying the heterogeneity of the current distribution ( $0 < \mathcal{H} < 1$ )      |
| $i_0$         | exchange current density ( $\text{A m}^{-2}$ )                                                                |
| $i_l$         | limiting current density ( $\text{A m}^{-2}$ )                                                                |
| $j$           | normal current density at the electrode surface ( $\text{A m}^{-2}$ )                                         |
| $\vec{j}$     | current density vector in the electrolyte ( $\text{A m}^{-2}$ )                                               |
| $\vec{J}$     | molar flux of soluble species ( $\text{mol m}^{-2} \text{s}^{-1}$ )                                           |
| $\vec{J}_s$   | current density vector in the solid phases ( $\text{A m}^{-2}$ )                                              |
| $k_0$         | rate constant ( $\text{m s}^{-1}$ )                                                                           |
| $L$           | length of the electrode–electrolyte interface in the 2-D representation (m)                                   |
| $l_c$         | channel length in the 2-D representation (m)                                                                  |
| $L_c$         | channel length in the 3-D honeycomb structure (m)                                                             |
| $n$           | number of electron(s) involved in the reaction                                                                |
| $\vec{n}$     | normal vector                                                                                                 |
| $n_c$         | number of channels of the 2-D representation                                                                  |
| $N_c$         | number of channels of the 3-D honeycomb electrode                                                             |
| $p$           | liquid pressure (Pa)                                                                                          |
| $R$           | molar gas constant ( $\text{J K}^{-1} \text{mol}^{-1}$ )                                                      |
| $R_A$         | surface area ratio between the positive and the negative electrodes                                           |
| $R_L$         | length ratio between the positive and the negative electrode–electrolyte interfaces in the 2-D representation |
| $S$           | section of the 3-D reactor in the (y,z) plane ( $\text{m}^2$ )                                                |
| $T$           | temperature (K)                                                                                               |
| $\vec{u}$     | electrolyte velocity vector ( $\text{m s}^{-1}$ )                                                             |
| $U$           | cell voltage (V)                                                                                              |
| $V$           | electronic potential in the solid phase (V)                                                                   |
| $v_{in}$      | inlet electrolyte velocity ( $\text{m s}^{-1}$ )                                                              |
| $z$           | valence of the ionic species                                                                                  |

### Greek letters

|            |                                                                             |
|------------|-----------------------------------------------------------------------------|
| $\alpha_o$ | anodic transfer coefficient (oxidation)                                     |
| $\alpha_r$ | cathodic transfer coefficient (reduction)                                   |
| $\eta$     | overpotential (V)                                                           |
| $\kappa$   | electrolyte conductivity ( $\text{S m}^{-1}$ )                              |
| $\mu$      | electrolyte dynamic viscosity ( $\text{Pa s}$ )                             |
| $\rho$     | electrolyte density ( $\text{kg m}^{-3}$ )                                  |
| $\phi$     | ionic potential (V)                                                         |
| $\nu_{ei}$ | number of electron involved in the reaction per mole of reactant or product |
| $\sigma$   | electronic conductivity of solid domains ( $\text{S m}^{-1}$ )              |

### Subscript

|     |                                                                              |
|-----|------------------------------------------------------------------------------|
| $i$ | Ionic species ( $i = \text{Pb}^{2+}, \text{H}^+, \text{CH}_3\text{SO}_3^-$ ) |
|-----|------------------------------------------------------------------------------|

### Superscript

|   |                                              |
|---|----------------------------------------------|
| + | quantity referring to the positive electrode |
| – | quantity referring to the negative electrode |

### Other

|                   |               |
|-------------------|---------------|
| $\langle \rangle$ | average value |
|-------------------|---------------|

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